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properties that are of value in the area of propulsion and missile signatures, as well as reactions within and on small particles that bear on the areas of decontamination and even the dispersal of agents. Research was undertaken on a number of major projects including studies of the formation and growth of clusters, photodissociation and energy transfer, and investigations to deduce the thermochemistry of clusters.

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THE AGGREGATED STATE OF MATTER: ELUCIDATING TRANSITIONS FROM THE
GAS TO THE CONDENSED PHASE AND THE FORMATION OF AEROCOLLOIDS

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Final Report

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THE AGGREGATED STATE OF MATTER: ELUCIDATING TRANSITIONS FROM THE GAS TO THE CONDENSED PHASE AND THE FORMATION OF AEROCOLLOIDS

ABSTRACT

Understanding the behavior of matter in a highly dispersed state whose properties are influenced by the finite dimensions of the system--aerosols or aerocolloidal media in the gas phase, fine particles, clusters or thin films at the surface, and colloids dispersed in liquids--is of considerable fundamental scientific interest, and at the same time bears on a number of applied areas of technological importance. From a scientific point of view, the work addresses a number of challenging problems with the prospect of advancing knowledge in the field of phase transformations, condensed matter and surfaces, and aerosol science. In terms of application to programs of interest to the U.S. Army, the research bears on problems of interest in the field of detection, obscuration by both natural and intentional methods of particle generation, the dispersal of agents, mechanisms of reactions that are involved in combustion and fast reactions in energetic materials, the formation and growth of small clusters and their optical properties that are of value in the area of propulsion and missile signatures, as well as reactions within and on small particles that bear on the areas of decontamination and even the dispersal of agents. Research was undertaken on a number of major projects including studies of the formation and growth of clusters, photodissociation and energy transfer, and investigations to deduce the thermochemistry of clusters.

SUMMARY OF ACCOMPLISHMENTS UNDER RECENT ARO SPONSORSHIP

Support from the U.S. Army Research Office for a proposal entitled "The Aggregated State of Matter: Elucidating Transitions from the Gas to the Condensed Phase and the Formation of Aerocolloids" commenced on August 15, 1985. Results of the ARO-sponsored program formed the basis of 56 publications and 97 presentations at scientific conferences and seminars.

The general strategy of this program was to characterize the properties of small clusters, which are the precursors to aerosol particles, as a method for exploring basic processes such as nucleation, condensation and the interaction of light with matter. The results provided insight into factors governing the size distribution and morphology of small particles produced in smoke and missile exhausts, as well as those resulting from natural phenomena such as fogs and hazes. Some of the more significant findings of the ARO-sponsored studies are very briefly outlined below. Details of these and other results are given in the publications; those completed papers which have not as yet appeared in print are included as appendices.

STUDIES OF THE FORMATION AND GROWTH OF CLUSTERS

In order to elucidate the mechanisms of formation and growth of clusters, as well as provide data for assessing nucleation processes occurring in supersonic expansions, we undertook investigations of clusters comprised of a number of different atomic and molecular constituents. An important aspect of these studies involves ionization of clusters and mass spectrometry of the resulting distributions. Knowledge of dissociation processes assists in interpreting the measurements of the cluster distributions, and is of interest in its own right as a contribution to understanding unimolecular dissociation mechanisms and energy transfer processes.

Dissociation Processes Following Nonresonant Multiphoton Ionization

We have studied the dynamics of dissociation of clusters upon multiphoton ionization by using time-of-flight mass spectrometry with a reflecting electric field. Systems that were examined include methanol, ammonia, and xenon clusters. Results for each are briefly discussed below.

Ammonia Clusters. Ammonia is an interesting system for study since it undergoes a well known "internal" ion-molecule reaction following ionization. The NH_4^+ cation is formed, and the hydrogen-bonded system undergoes substantial rearrangement around the newly formed charged center. A study of the extent of dissociation in ionized ammonia clusters was performed and reported earlier (1-3). Under the current ARO sponsorship the timescales of dissociation were more carefully investigated. Dissociation rates were found to be time dependent as a result of a cooling with time of the cluster ensemble via "evaporation". If dissociation is observed shortly after ionization (on the order of one microsecond), dissociation rates are about 10^5 sec^{-1} with no particular trend in cluster size. However, when observed over longer times (10-100 μsec), average rates are found to be slower (about 10^4 sec^{-1}) and generally increase with cluster size (from 10 to 25 molecules). See Figure 1. The cluster size that is observed is most likely not the initial size of the neutral cluster since prompt dissociation (within a tenth of a microsecond or so) occurs. Therefore, the observed dissociation rates should depend upon expansion conditions due to variations in the internal energy distribution of the ionized clusters; these variations are a result of the different contributions from larger clusters that rapidly dissociate to the size in question. This effect also probably explains the temperature dependence of dissociation rates of ionized argon clusters observed by Märk and coworkers (4). The role of laser fluence in dissociation is seen by comparing trends in the cluster sizes as seen in Figures 2a and 2b. These data were taken under identical expansion conditions. Further details are given in Appendix A.

Methanol Clusters. Ionized methanol undergoes a proton transfer reaction, leading to the formation of protonated clusters with methanol (5). The methanol system is of particular interest

since other possible reaction channels are available. Figure 3 (Spectrum 1 in Table I) shows a conventional time-of-flight mass spectrum of methanol clusters obtained by multiphoton ionization (at 266 nm). A sequence of ions (labelled A) of the form $H^+(CH_3OH)_n$ are observed. Another sequence (labelled B) of the form $H^+(H_2O)(CH_3OH)_n$ also begins to appear at about seven methanol units. In Figure 4 (Spectrum 2 in Table I), the spectrum of only daughter ions is shown (parent ions were not reflected). Several series of peaks are apparent. The mass loss is determined by the time-of-flight and also by the threshold potential required for reflection. The A labelled series represents the loss of one methanol molecule (32 daltons) from an ion that enters the field-free region as $H^+(CH_3OH)_n$. Series B results from the loss of one methanol molecule from the species $H^+(H_2O)(CH_3OH)_n$. Series C derives from a mass loss of 78 daltons from $H^+(CH_3OH)_n$ where the mass loss corresponds to the loss of both a methanol and dimethyl ether molecule. Peak D corresponds to the loss of a mass of 18 daltons (H_2O) from $H^+(CH_3OH)_2$. Series E results from the reflection of a small portion of the undissociated ions on the low energy side of the birth potential distribution. By further reduction of the reflecting potentials, the shoulders on the early arrival side can be resolved and reveal more extensive methanol evaporation, e.g., the loss of up to five methanol molecules from the protonated octamer.

The spectra suggest several dissociative processes. First, ionization leads to a rapid internal (intracluster) proton transfer reaction to produce $H^+(CH_3OH)_n$ followed by the slower evaporative unimolecular dissociation processes, as has been observed earlier for ammonia clusters (1). The protonated dimer is seen to eliminate water to produce protonated dimethyl ether. This process requires at least several tenths of a microsecond since little or no $(CH_3)_2OH^+$ is observed in the conventional TOF spectrum. The gas-phase analogue of this reaction (between protonated methanol and methanol) is also known (5). Details of this observation have been published (6). For the larger clusters, however, C_2H_6O elimination occurs and leads to the production of $H^+(H_2O)(CH_3OH)_n$. As opposed to the protonated methanol dimer, water evidently is retained in

the cluster ion since H_3O^+ is more strongly solvated by methanol than is $(\text{CH}_3)_2\text{OH}^+$. Furthermore, this process occurs on the order of one to twenty microseconds for clusters of less than 8 molecules (as suggested by series C in Figure 4), but requires less than two microseconds for larger clusters (as indicated by the appearance of series B in Figure 4). These processes and their timescales are summarized in Table I. A paper describing these results on the larger clusters is currently in press. See Appendices B and C.

Xenon Clusters. We have conducted a multiphoton ionization (at 266 nm) study of atomic xenon clusters for comparison with the dissociation of molecular systems. The relative cluster abundances for the system Xe_n^+ are found to be virtually identical with those obtained by high-energy electron impact ionization, and dissociation is indicated as a factor in the formation of magic numbers in the cluster distributions; see Figure 5. This observation indicates the importance of the energy liberated following ionization of the cluster in effecting the magic numbers and size distribution of weakly bound clusters as compared to the energy deposited to initiate ionization. The peak shapes of the Xe_2^+ , Xe_3^+ , and Xe_4^+ in the time-of-flight spectra under single field acceleration exhibited tails toward longer flight times which are the result of rapid dissociation of larger clusters. No tail is apparent in the Xe^+ peak or for clusters larger than Xe_4^+ . From these results, the dissociation of larger clusters to Xe_4^+ , Xe_3^+ , and Xe_2^+ is found to occur in the neighborhood of hundredths of microseconds. These are evidently the only species which have metastable contributions in the time domain accessible by this method. Dissociation for clusters of ten or more atoms have been reported (7) on slower timescales; further details are given in the publication of this work (8).

Dissociation of Ionized Clusters Through Rotational Tunneling

We have observed metastability of Ar_3^+ on a timescale that is too long to be accounted for by vibrational predissociation. On the basis of observations in our laboratory as well as others, we

have shown that tunneling through rotational barriers can explain these unexpectedly long timescales. Our experimental findings are in good accord with calculations we have made using a WKB approximation. An interesting result is that for a fixed rotational state, L , tunneling is insensitive to mass which suggests this may be a general phenomenon in cluster dissociation processes. See Reference 9 for further details.

Cluster Spectroscopy. In order to establish the ability to ascertain the degree of aggregation of a system to which a given species is attached, measurements were undertaken on clusters of various molecules bound with a test chromophore, phenylacetylene. Extensive experiments were carried out for clusters comprised of CO_2 and ammonia. The small spectral (red) shifts in the case of CO_2 provided evidence for the assignment of the geometry of these clusters corresponding to a CO_2 bound to the acetylenic hydrogen of the phenylacetylene. Of particular interest were experiments with ammonia which displayed quite different spectroscopies when the phenylacetylene was co-expanded with ammonia compared to ones made in which a cross-beam effusive source was used to deposit a phenylacetylene molecule on a preexisting ammonia surface. These results were quite exciting and revealing in that they established that it is possible to ascertain the degree of aggregation of a system to which a chromophore is bound through resonance enhanced ionization. This offers the promise that in favorable cases it is possible to ascertain whether a given molecule is adsorbed on a cluster surface or contained as an embedded molecule within a "small microscopic droplet". These recent findings truly establish the surface cluster analogy. See Appendix D.

Investigation of the Stabilities of Neutral and Ionic Lead and Lead-Antimony

Clusters Under Single and Multiphoton Ionization Conditions

Investigations of metal clusters were performed to gain further insight into cluster formation processes. A gas aggregation source was used to produce the species and time-of-flight laser ionization was utilized in their detection. The fluence dependence of lead cluster ion

distributions at 222 nm and 308 nm reveal markedly different behavior. Results obtained at 308 nm display a simple uniform increase in intensity with higher laser fluence with little change in relative intensities. At 222 nm, however, a significant transformation is found from a markedly different low fluence distribution to a high fluence pattern, which is essentially indistinguishable from that observed at 308 nm. It is concluded that mass spectra obtained at 308 nm, regardless of fluence, or at 222 nm and high fluence contain appreciable contributions from fragmentation. Hence, under these conditions the mass spectra are found to be dominated by cluster ion stabilities.

Magic numbers observed at both high and low fluence correspond well to those obtained using electron-impact ionization, and in many instances parallel the magic numbers characteristic of rare-gas clusters. This suggests the stabilities of both neutral and monovalent cationic lead clusters are largely determined by close-packing considerations, and are not appreciably influenced by electronic structure. Similar preferences for close-packed structures are also found for mixed lead-antimony clusters containing one or two antimony atoms that are ionized using high fluence 308 nm excitation. See Appendix E.

PHOTODISSOCIATION AND ENERGY TRANSFER

Studies of cluster dissociation following photon absorption yield data of interest in understanding energy transfer in systems having widely disparate modes. The results also provide information on cross sections for photodissociation and findings of differences in dissociation with varying degrees of solvation bear on photochemical processes in the condensed state.

Kinetic Energy Release in Photodissociation of Cluster Ions

The kinetic energy release in the photodissociation of CO_3^- hydrates and the SO_2 dimer anion has been examined (10). The photodissociation experiments on $\text{CO}_3^-(\text{H}_2\text{O})_n$ ($n=1$ to 3) yield results which suggest that all three hydrated ions undergo photodissociation by the same mechanism. Dissociation is found to proceed via absorption of a photon by CO_3^- into an electronic

excited state that is only slightly perturbed by the presence of the water molecules. Hydration totally eliminates the dissociation channel to O^- which dominates in the case of the bare anion. For each of the hydrates, more of the available energy is found to be partitioned into relative translation than is expected based on statistical phase space theory. See Figure 6. Photodissociation of $(SO_2)_2^-$ similarly resulted in more kinetic energy release than expected; see Figure 7. Through examination of the kinetic energy release in $(SO_2)_2^-$ with parallel and perpendicularly polarized light, the lifetime of the excited complex against dissociation was determined to be less than one rotational period.

Photodissociation of Argon Trimer Cation

As part of our work on rare gas clusters, we recently undertook a determination of the photodissociation spectrum of Ar_3^+ over the wavelength range of 539 to 620 nm (the range of rhodamine/6G) (11). The spectrum displays a peak in cross-section near 544 nm with the photoproduct being Ar^+ , which has been found to be dependent on the expansion conditions; see Figure 8. More recently, we have been reexamining the photodissociation and extending the measurements into the blue in light of some recent results from Lineberger's group at the University of Colorado. The absolute cross-section at 544 nm is $2.5 \times 10^{-16} \text{ cm}^2$ as determined by both parent ion disappearance and product ion appearance. Preliminary results indicate a second peak around 523 nm in accord with the observations of Lineberger and coworkers (544 nm peak was observed only as a shoulder in their study). Indications are that the rather narrow 544 nm peak is the result of a $\Sigma_g^+ \leftarrow \Sigma_u^+$ bound-state transition whereas the broader 523 nm peak is the result of a transition to a repulsive Π_g state. The relative contributions of these two transitions depends on the method of cluster production.

THERMOCHEMISTRY OF CLUSTERS

We have undertaken extensive studies of the thermochemistry of selected cluster ions. These data are useful in assessing the role of cluster properties in effecting the energy barrier to nucleation and also provide valuable information on the thermochemical differences between ions in the gaseous and condensed state (12,13). The data also find value in understanding factors governing the stability of clusters and their structure. During the grant period, work has been undertaken on metal cations, such as Bi^+ and K^+ , and anions including Cl^- and PO_3^- . See Appendix F.

Gas Phase Hydration of Monomeric Metaphosphate Anion

The monomeric metaphosphate ion is of extensive interest in biological processes and also is an important intermediate in the oxidation and subsequent formation of aerosols generated by the combustion of phosphorus. Currently there is considerable controversy concerning its behavior upon hydration. Recently, we have completed a study via high pressure mass spectrometry on the clustering of water onto the monomeric metaphosphate ion PO_3^- . The ion is produced from electron attachment to phosphoric acid. Beyond the first hydration step, it was necessary to use D_2O in order to avoid interference from the hydrates of HCO_3^- , which appeared at the lower temperatures and higher water vapor concentrations required to examine the further clustering steps. The enthalpy changes for the first four stepwise additions of D_2O to PO_3^- were determined to be -12.6, -11.4, -16.3, and -11.0 kcal/mol, respectively. The enthalpy value of -12.6 kcal/mol compares well with the value of -12.9 kcal/mol obtained for the addition of H_2O onto PO_3^- . The respective entropy changes are -20.7, -22.1, -36.4, and -22.6 cal/K-mol and the respective standard free energy changes are -6.4, -4.8, -5.4, and -4.3 kcal/mol. This system was unusual in that the magnitude of the enthalpy and free energy changes of the third hydration step are found to be larger (more negative) than those of the previous two steps. The values of the first two hydration steps

are consistent with simple adduct formation, whereas the unusual result for the third step suggests that an isomerization into the dihydrogen orthophosphate ion $(HO)_2PO_2^-$ may have occurred. Transformation of ions at a particular degree of hydration are known as in the case of the hydration of NO^+ where the fourth hydration step leads to the formation of $H_3O^+(H_2O)_2$. The isomerization may proceed due to a lowering of an energy barrier upon hydration or due to a larger solvation energy for the orthophosphate ion. Reference 14 details the implications of the results.

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FIGURE CAPTIONS

Figure 1. Rate of evaporative unimolecular dissociation of ammonia cluster ions versus size of the cluster, N.

Figure 2(a). Time-of-flight spectrum of protonated ammonia cluster ions. $\text{NH}_4^+(\text{NH}_3)_4$ is the prominent peak at 20.0 μs . For this spectrum $\lambda = 266 \text{ nm}$, $P_0 = 800 \text{ torr NH}_3$ neat, focusing lens position = 18.5 cm (weakly focused).

Figure 2(b). Time-of-flight spectrum of protonated ammonia ion clusters. $\text{NH}_4^+(\text{NH}_3)_4$ occurs at 20.0 μs . For this spectrum $\lambda = 266 \text{ nm}$, $P_0 = 800 \text{ torr NH}_3$ neat, focusing lens position = 9.75 cm (tightly focused).

Figure 3. Conventional time-of-flight mass spectrum of methanol clusters by multiphoton ionization at 266 nm. Series A = $\text{H}^+(\text{CH}_3\text{OH})_n$; Series B = $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{OH})_n$.

Figure 4. Spectrum of dissociation product ions. Series labels described in text. The sizes of the precursor ion $\text{H}^+(\text{CH}_3\text{OH})_n$ (for Series A, C, D, and E) and $\text{H}^+(\text{H}_2\text{O})(\text{CH}_3\text{OH})_n$ (for Series B) are indicated.

Figure 5. Intensity of Xe_n^+ versus time of flight. The source condition was 900 torr and ionization was made in a two-field time-of-flight lens using 266 nm photons. The intensity scale is enlarged in the insert to display the features for cluster sizes greater than 22.

Figure 6. Integrated probability distributions for kinetic-energy release in the photodissociation of the CO_3^- hydrates, (a) $\text{CH}_3^-(\text{H}_2\text{O})$, (b) $\text{CO}_3^-(\text{H}_2\text{O})_2$, (c) $\text{CO}_3^-(\text{H}_2\text{O})_3$. Dotted curves from statistical phase space theory. Solid lines are experimental measurements.

Figure 7. Integrated probability distribution for kinetic-energy release in the photodissociation of $\text{SO}_2^-(\text{SO}_2)$. Dotted curves from statistical phase space theory. Solid lines are experimental measurements.

Figure 8. Influence of beam expansion conditions on the photodissociation of Ar_3^+ . The data plotted as black squares (■) were taken under the best expansion conditions (coldest beam), the black circles (●) were next coldest, and the open squares (□) the warmest. The error bars represent one standard deviation.

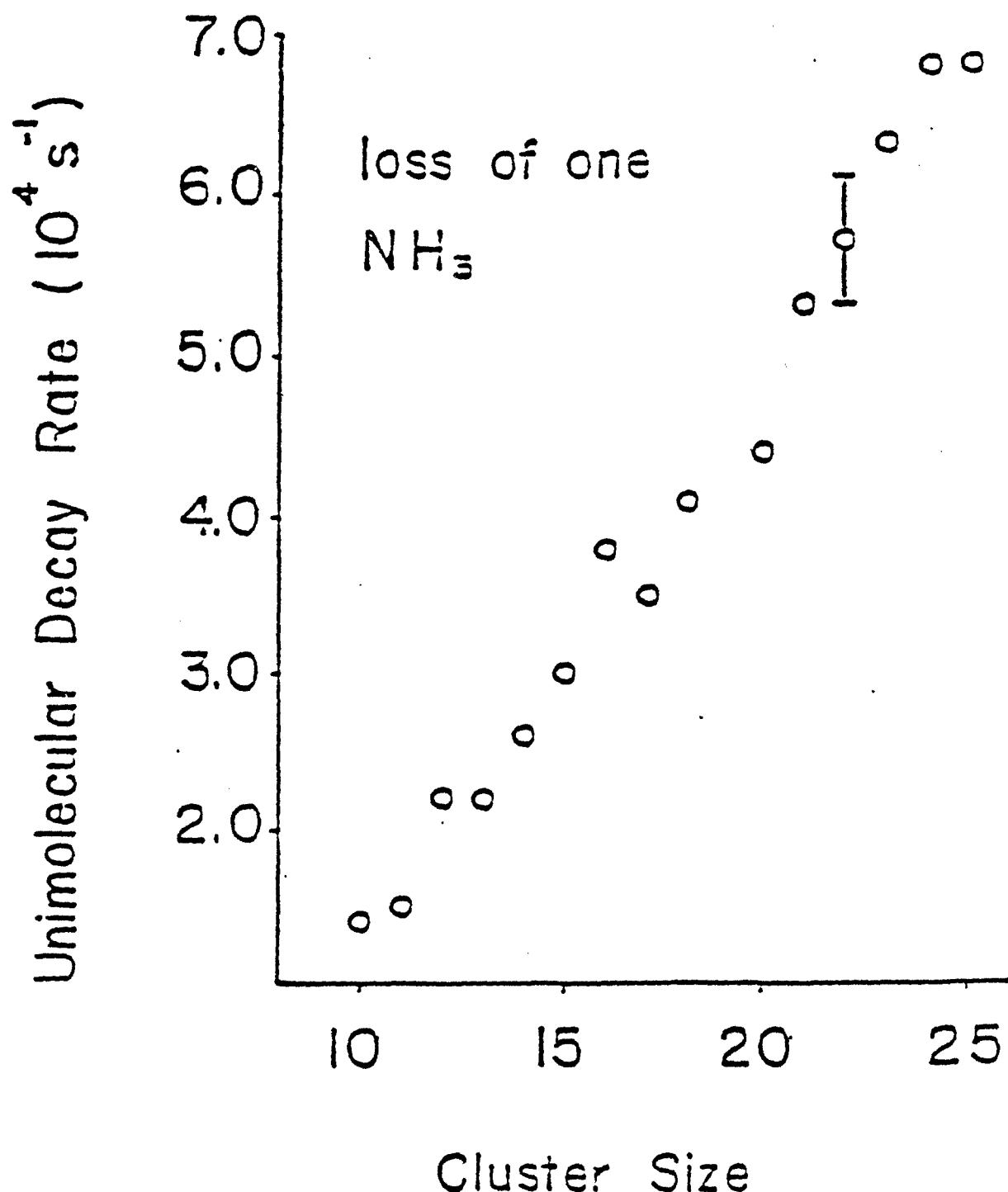


Figure 1

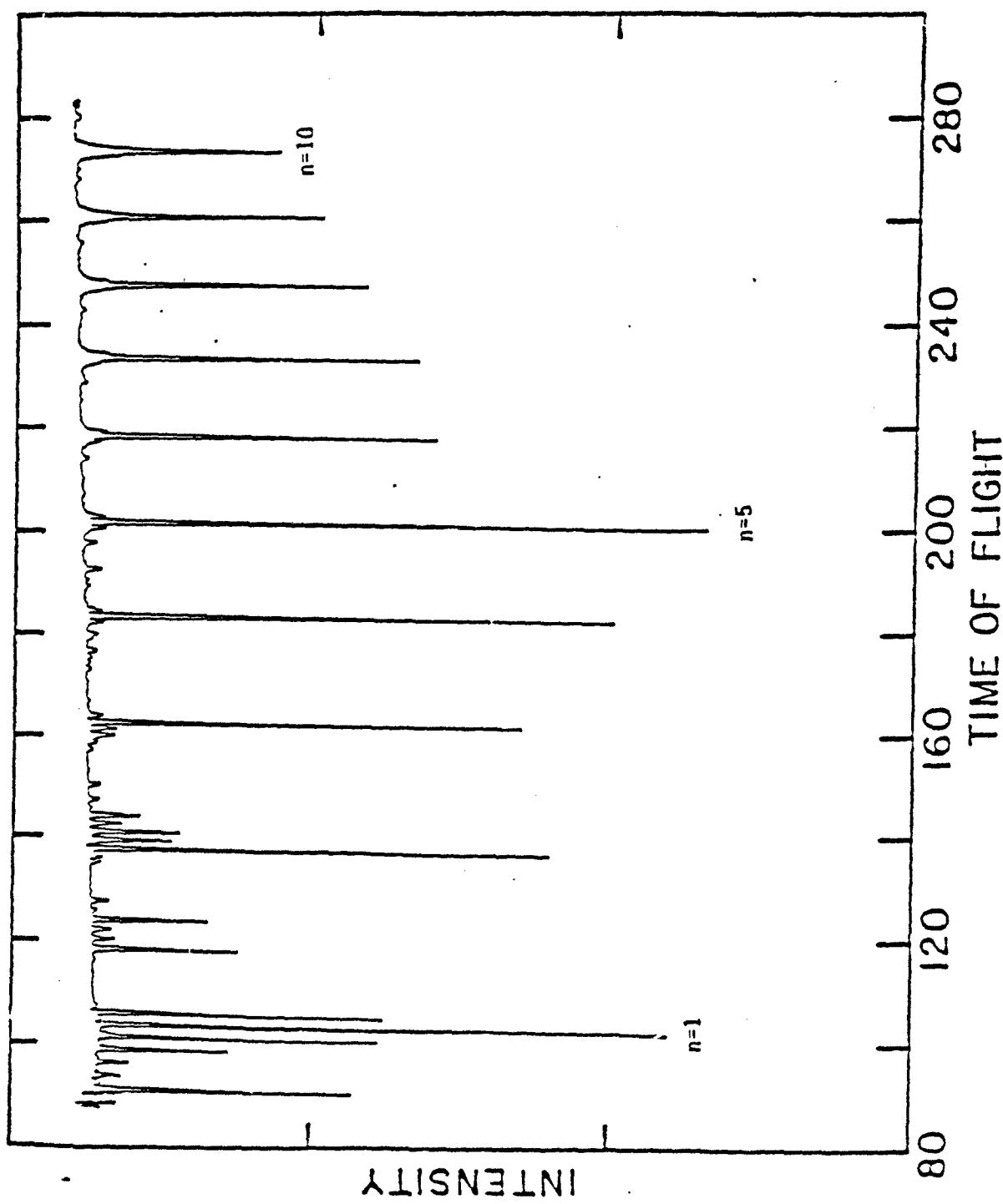


Figure 2a

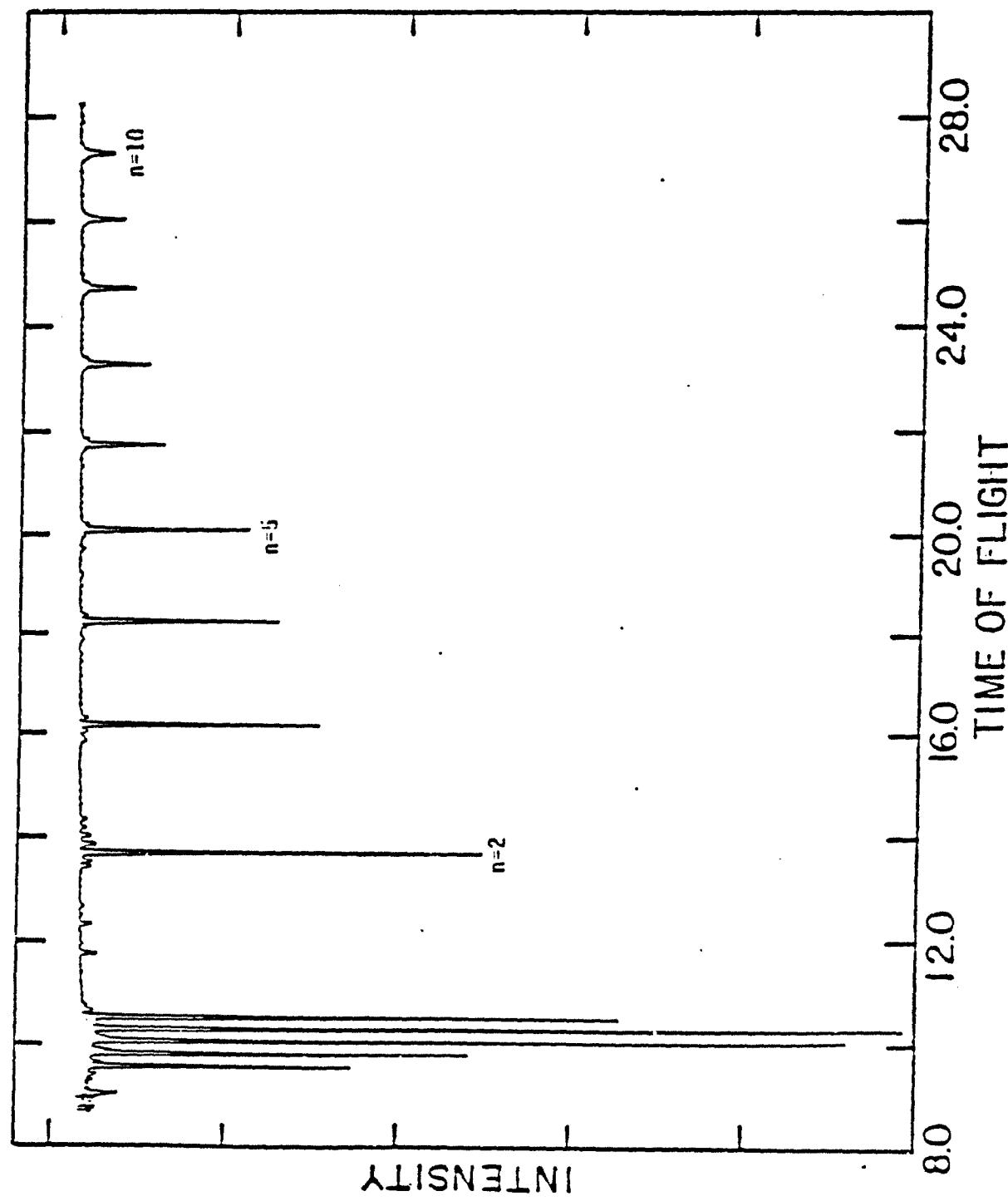


Figure 2b

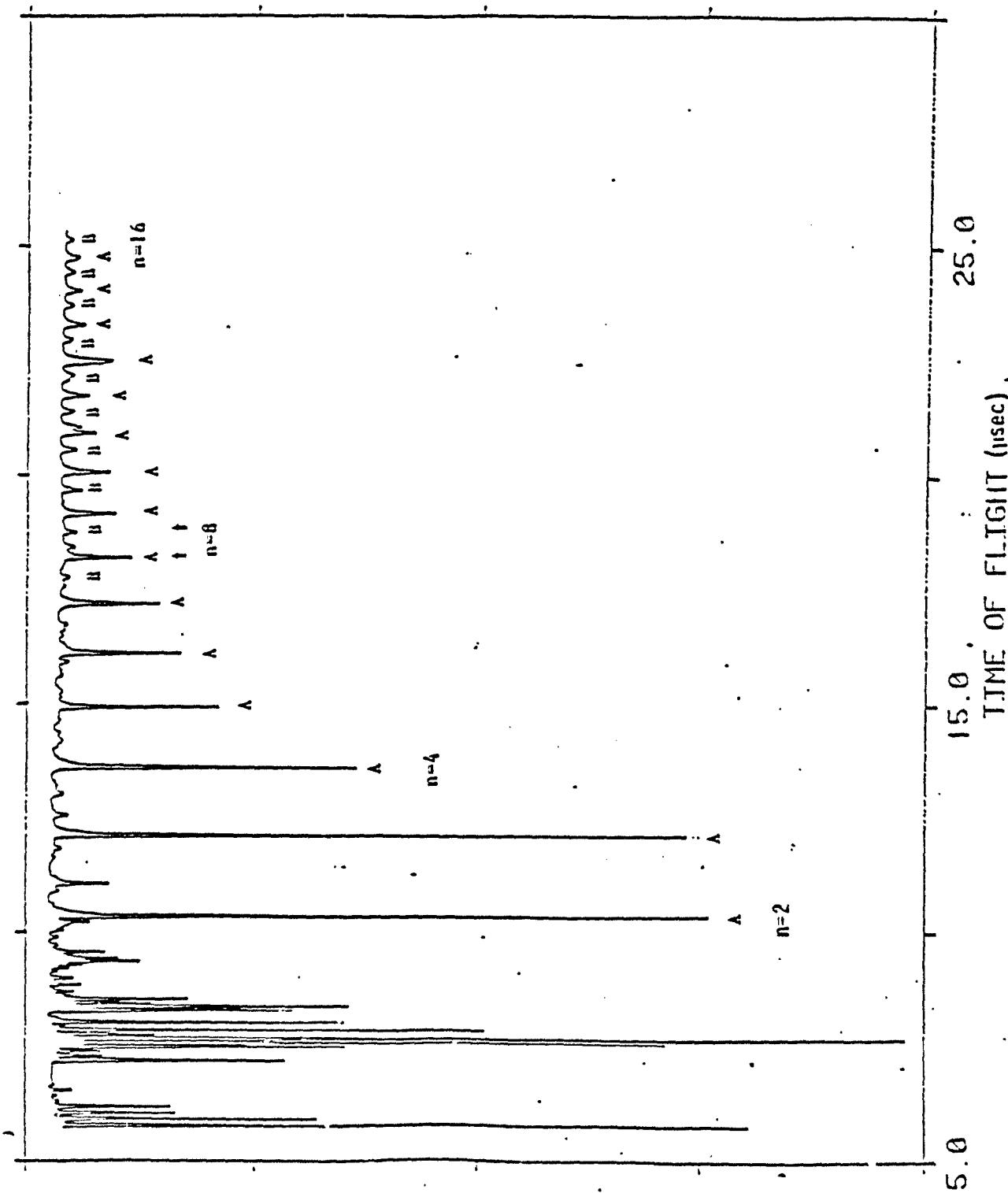


Figure 3

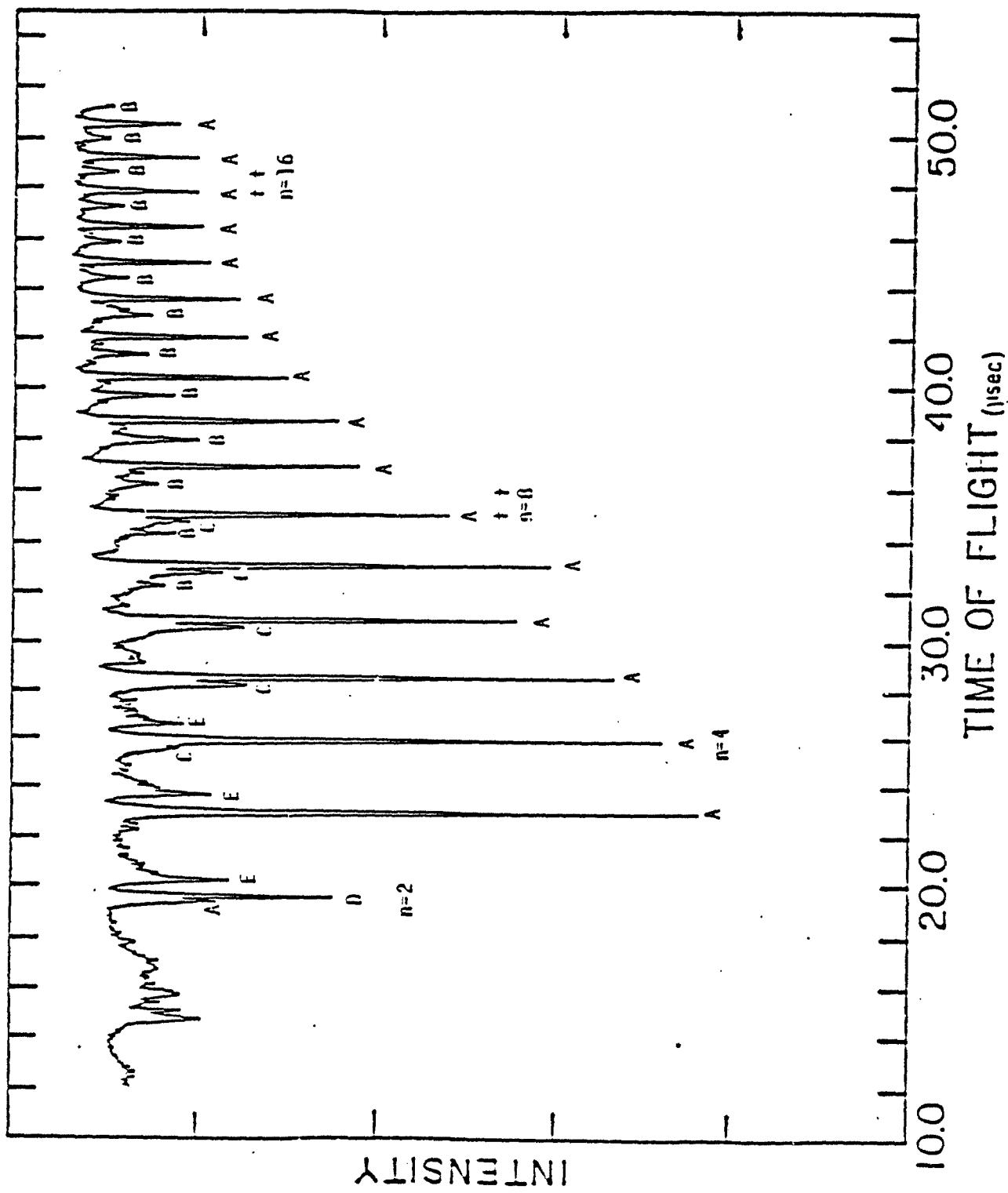


Figure 4

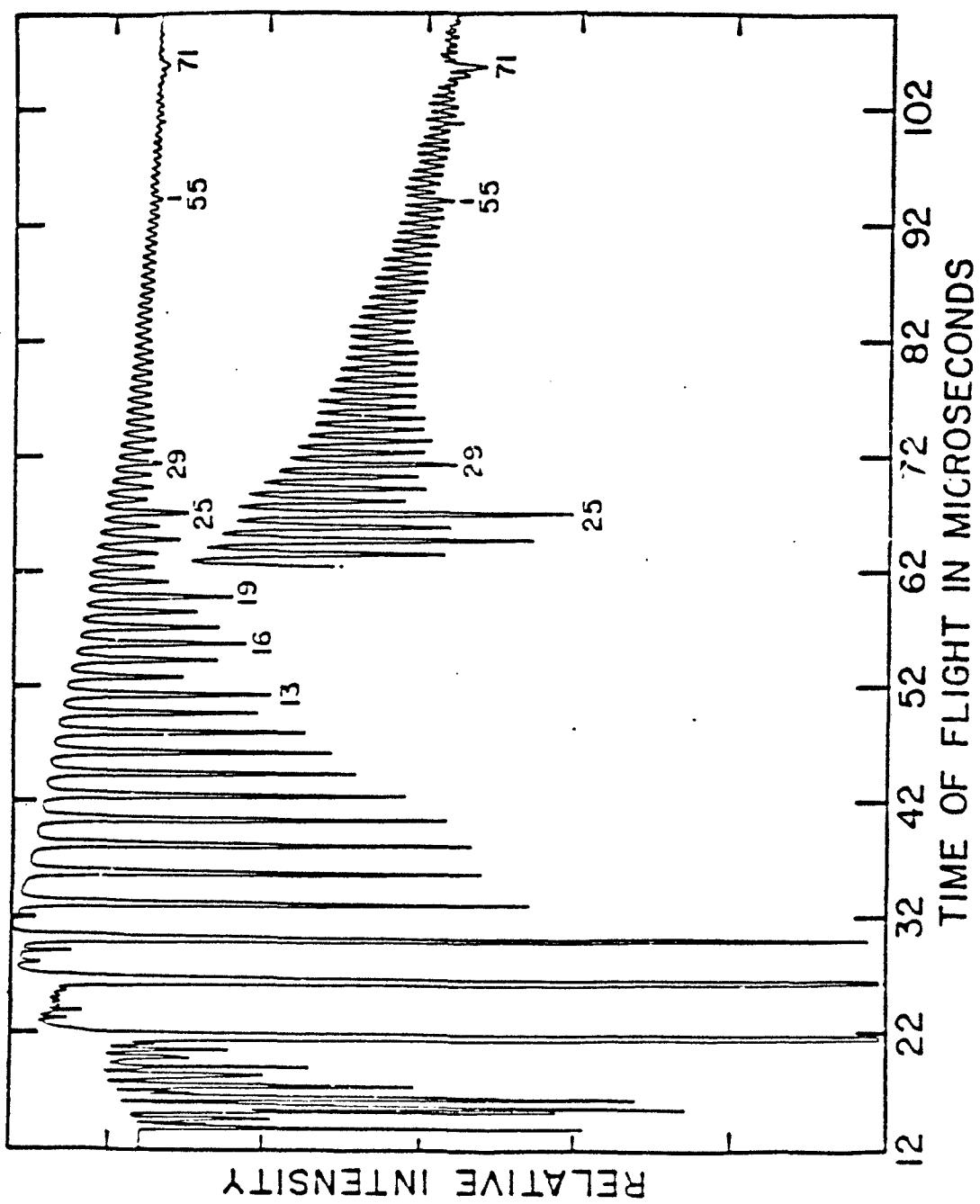


Figure 5

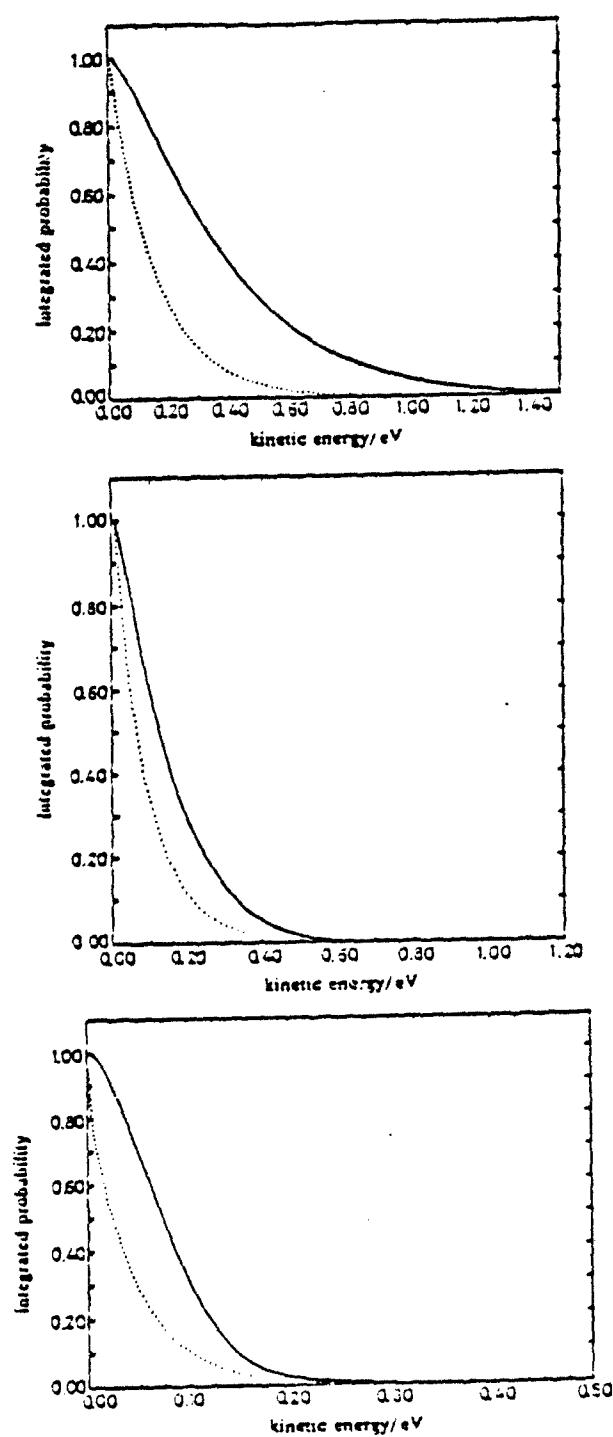


Figure 6

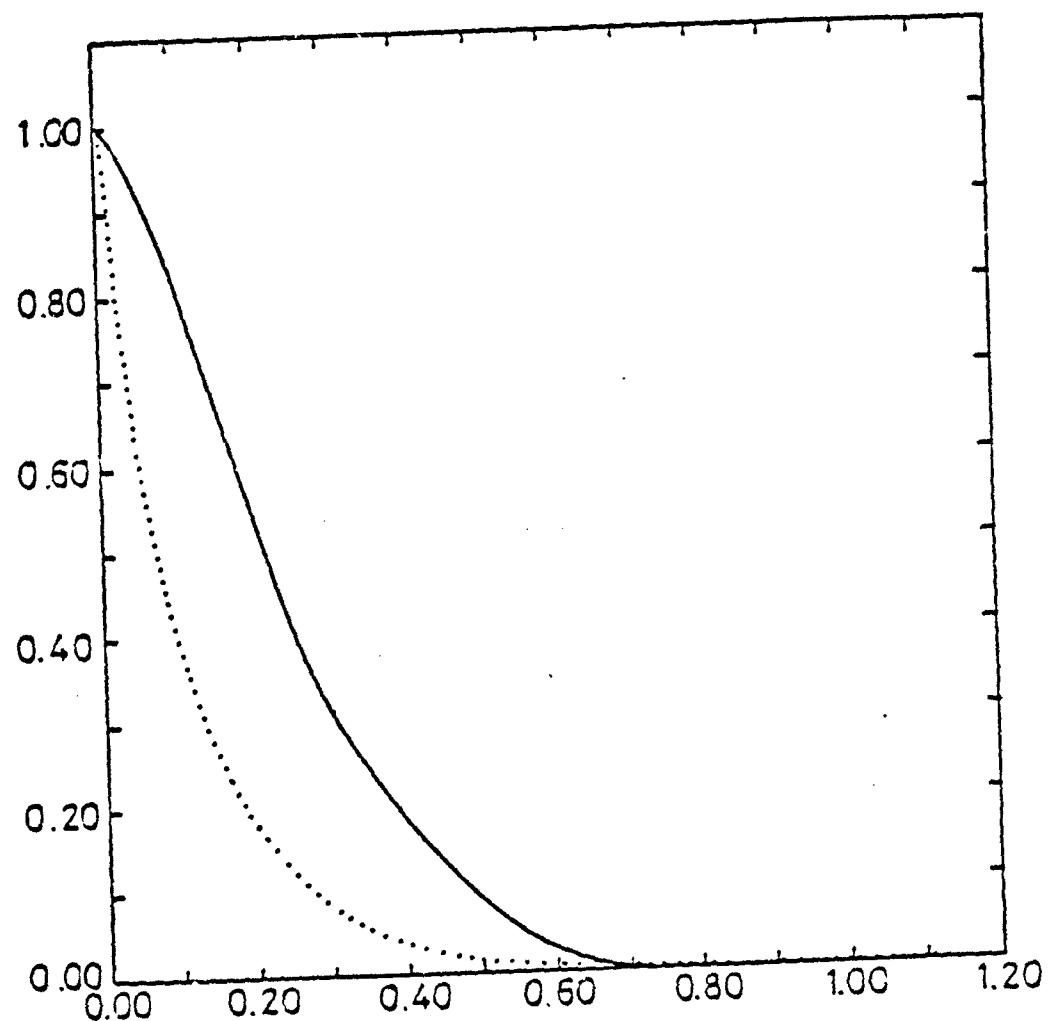


Figure 7

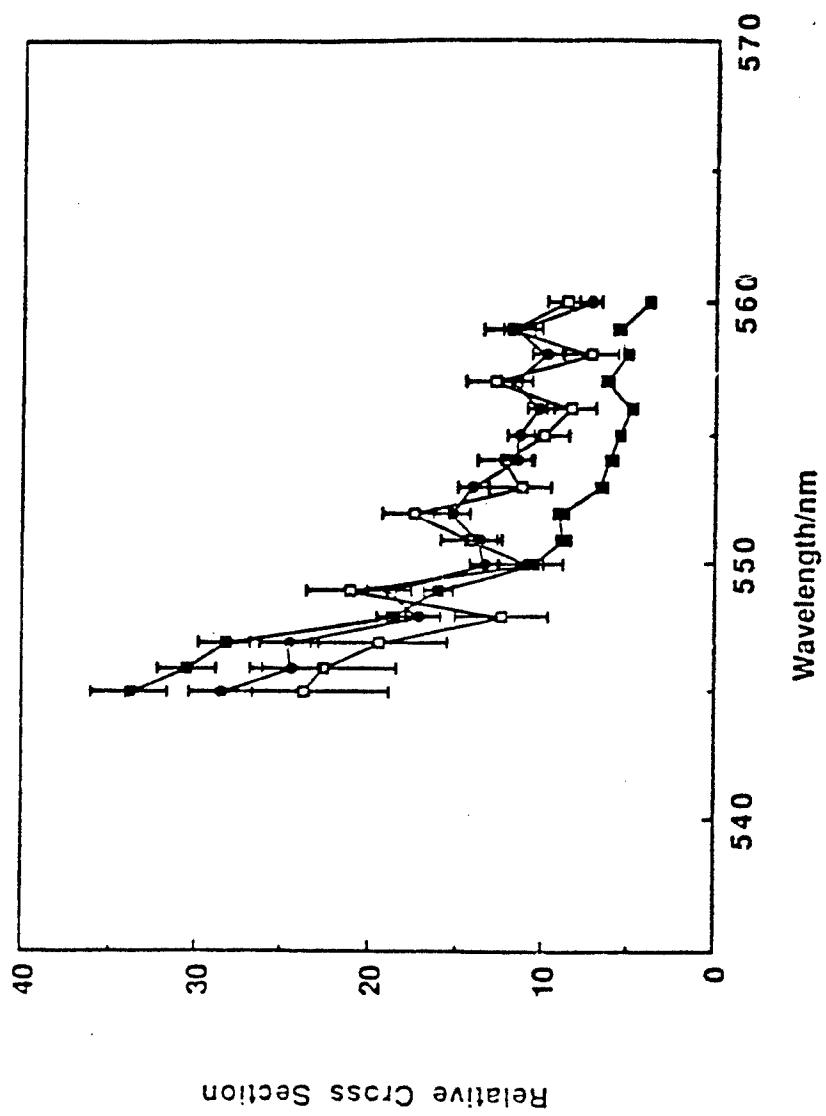


Figure 8

Table I
Dissociation Processes of Methanol Clusters
Following Multiphoton Ionization

Process	Observed Timescale (nsec)	Spectrum/ Peak
$\{(\text{MeOH})_n\}^*$	$\text{H}^+(\text{MeOH})_{n-1} + \text{MeOH}$	<1 to 2 1-A
$\{\text{H}^+(\text{MeOH})_2\}^*$	$\text{H}_2\text{O}^+ + \text{H}_2\text{O}$	>1 to 8 2-B
$\{\text{H}^+(\text{MeOH})_n\}^*$	$\text{H}^+(\text{MeOH})_{n-m} + \text{mMeOH}$ (m up to 5 for n=8)	1 to 25 2A (m=1)
$\{\text{H}^+(\text{MeOH})_n\}^*$	$\text{H}^+(\text{H}_2\text{O})(\text{MeOH})_{n-3} + \text{H}_2\text{O} + \text{MeOH}$	>1 to 20 (n=4 to 9) <2 (n>10) 2-C 1-B
$\{\text{H}^+(\text{H}_2\text{O})(\text{MeOH})_n\}^*$	$\text{H}^+(\text{H}_2\text{O})(\text{MeOH})_{n-1} + \text{MeOH}$	~ 1.5 to 25 2-B

SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT:

J. J. Breen, Research Assistant
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Degrees Conferred:

J. J. Breen, Ph.D., 1988
S. Morgan, Ph.D., 1988
R. W. Farley, Ph.D., 1988

LIST OF PUBLICATIONS SPONSORED BY ARO SINCE BEGINNING OF GRANT PERIOD, AUGUST 15, 1985

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Dissociation of Ammonia Cluster Ions Following Their Formation Via Multiphoton Ionization

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ABSTRACT

Using a time-of-flight mass spectrometer equipped with a reflectron, unimolecular (evaporative) dissociation rate constants of ammonia cluster ions were measured as a function of cluster size, n , ($4 \leq n \leq 18$) at both early and late times following their production via multiphoton ionization. The rates measured in early time windows are considerably higher than those determined for later times; although they show no specific trend with cluster size, there is a general decrease in magnitude with size for ionization at 355 nm. By contrast, those measured at later times invariably display an appreciable dependence on cluster size, where the rates rise from 1.1×10^3 to $1.4 \times 10^4 \text{ sec}^{-1}$ as n increases from 4 to 18. The dissociation rates for clusters comprised of ND_3 and NH_3 are nearly the same within the combined experimental errors of the rates measured for the two individual systems. Nevertheless, those for ND_3 are consistently slightly larger than those for NH_3 . Although the early time results displayed some minor dependence on laser power, those at longer times did not. Findings concerning the trends of rates are discussed in terms of statistical considerations of unimolecular decomposition in conjunction with thermochemical data available for the ammonia system.

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Reactions of Methanol Clusters Following Multiphoton Ionization

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ABSTRACT

Clusters of methanol formed in a supersonic expansion are subjected to multiphoton ionization (MPI) at 266 nm using a pulsed Nd:YAG laser. The resulting cluster ions, $H^+(CH_3OH)_n$, are found to undergo several introcluster reaction pathways which display a dependence on the degree of aggregation. In addition to the evaporative loss of methanol monomers at all sizes, and the loss of H_2O from the protonated dimer, it is found that a channel corresponding to $(CH_3)_2O$ and CH_3OH loss, with H_2O retention, also occurs. For clusters comprised of 4 to 9 methanol molecules, the $(CH_3)_2O$ elimination is observed to take place over the time window of about 1 to 15 μ sec after ionization, while prompt $(CH_3)_2O$ elimination also occurs in the size range above $n=7$. The mechanisms are considered in terms of estimated energetics for the various pathways.

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DISSOCIATION DYNAMICS OF METHANOL CLUSTERS FOLLOWING MULTIPHOTON IONIZATION

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ABSTRACT

Following multiphoton ionization (MPI), neutral methanol clusters are found to undergo a well known ion-molecule reaction which leads to the production of protonated clusters. Evaporative dissociation rates of the cluster ions are measured for sizes ranging from the dimer to the 21-mer following MPI. There is a general trend of the rates decreasing with time after the initial ionization event in accordance with the evaporative ensemble model. Rates measured at long times after ionization display a consistent trend of increasing with cluster size. These findings are shown to be in accord with statistical considerations of evaporative unimolecular dissociation. Collision induced dissociation cross sections are found to generally increase with size; the finding of a local minimum in the value for $H^+(CH_3OH)_3$ is in agreement with predictions of its structure. Finally, through a combination of unimolecular evaporative and collision-induced dissociation processes, as many as five methanol monomers are found to be lost from a cluster as small as $H^+(CH_3OH)_7$.

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PHOTOABSORPTION AND PHOTOIONIZATION OF CLUSTERS

R. G. Keesee and A. W. Castleman, Jr.

1. INTRODUCTION

Research into the formation and properties of clusters is a rapidly expanding endeavor. This book and several other recent volumes (1-4) are examples of the activity and breadth of this effort. Several motivations and technological advancements are responsible for this burst of activity. An early and continuing motivation is the recognition that clusters offer a means by which to bridge the gap between the gaseous and condensed phase so that the details of condensation and nucleation phenomena can be probed at the molecular level (5-7). A subject of interest in chemical kinetics concerns the avenues and rates by which energy is transferred and distributed within a system following an excitation process. Clusters are particularly valuable in such studies. The high frequency intramolecular modes versus the much lower frequency intermolecular modes of a cluster allow investigation of the coupling of modes of widely different energies. Furthermore, the number of degrees of freedom in the system can be increased by increasing cluster size without changing the chemical units of the system.

The present chapter addresses two areas of active research in the authors' laboratory. In Section 3, the results of spectroscopic studies via resonantly enhanced multiphoton ionization with time-of-flight mass spectrometry are described. One of the goals of spectroscopic studies of gas-phase clusters is to probe how the clustering environment and its extent affect the electronic and vibrational structure of a molecule within a cluster. One facet of these studies concerns the evolution, as the cluster increases in size, of spectral features that are associated with the respective condensed phase. Another important aspect is that the nature of intermolecular interactions can be studied. Section 4 deals with the chemistry and dissociation dynamics that accompany photoionization and Section 2 presents the experimental techniques.

2. EXPERIMENTAL METHODS

The experimental methods employed in the authors' laboratory for the study of spectroscopy, photophysics, and photochemistry of clusters employ gas expansion through a pulsed nozzle, multiphoton ionization, and time-of-flight mass spectrometry. The overall instrument is depicted in Figure 1. The apparatus consists of a translatable pressurized (several

MPa) cylindrical nozzle, a pulsed nozzle, and a fully flexible expansion tube.

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**INVESTIGATION OF THE STABILITIES OF NEUTRAL AND IONIC LEAD
AND LEAD-ANTIMONY CLUSTERS UNDER SINGLE AND MULTIPHOTON
IONIZATION CONDITIONS**

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ABSTRACT

The fluence dependence of lead cluster ion distributions at 222 nm and 308 nm reveal markedly different behavior. Results obtained at 308 nm display a simple uniform increase in intensity with higher laser fluence with little change in relative intensities. At 222 nm, however, a significant transformation is found from a markedly different low fluence distribution to a high fluence pattern, which is essentially indistinguishable from that observed at 308 nm. It is concluded that mass spectra obtained at 308 nm, regardless of fluence, or at 222 nm and high fluence contain appreciable contributions from fragmentation. Hence, under these conditions the mass spectra are found to be dominated by cluster ion stabilities.

Magic numbers observed at both high and low fluence correspond well to those obtained using electron-impact ionization, and in many instances parallel the magic numbers characteristic of rare-gas clusters. This suggests the stabilities of both neutral and monovalent cationic lead clusters are largely determined by close-packing considerations, and are not appreciably influenced by electronic structure. Similar preferences for close-packed structures are also found for mixed lead-antimony clusters containing one or two antimony atoms that are ionized using high fluence 308 nm excitation.

APPENDIX FSubmitted to J. Am. Chem. Soc.**The Hydration of Monomeric Metaphosphate Anion
in the Gas Phase****R. G. Keesee and A. W. Castleman, Jr.**

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ABSTRACT

Thermochemical data for the clustering of water molecules onto the monomeric metaphosphate anion PO_3^- in the gas phase are derived from a study by high pressure mass spectrometry. Experimental details are described and the enthalpy and entropy changes for the successive addition of the first four water (D_2O) molecules are reported. The results indicate that PO_3^- undergoes simple adduct formation up to the second hydration step, but the third hydration step involves an isomerization of the ion-water cluster into the dihydrate of the dihydrogen orthophosphate anion.